

4. PRODUCTION, IMPORT, USE, AND DISPOSAL

4.1 PRODUCTION

Arsenic is the 20th most abundant element in the earth's crust. It occurs most often as the sulfide in a variety of complex minerals containing copper, lead, iron, nickel, cobalt, and other metals (Merck 1989; US Fish and Wildlife Service 1988).

Arsenic is presently obtained as a byproduct of the smelting of copper, lead, cobalt, and gold ores. Arsenic trioxide is volatilized during smelting and accumulates in the flue dust, which may contain up to 30% arsenic trioxide. The crude flue dust is further refined by mixing with small amounts of galena or pyrite to prevent the formation of arsensites and roasting to yield a arsenic trioxide of 90–95% purity. By successive sublimations, a purity of 99% can be obtained. Arsenic metal can be prepared by the reduction of arsenic oxide with charcoal. Demand for metallic arsenic is limited and thus about 95% of arsenic is marketed and consumed in combined form, principally as arsenic trioxide which is subsequently converted to arsenic acid (Carapella 1992; Hanusch et al. 1985; USGS 1998b).

Since 1985, when the ASARCO smelter in Tacoma, Washington ceased operation, there has been no domestic production of arsenic and consequently, the United States remains entirely dependent on imports (USGS 1998b; U.S. Bureau of Mines 1988, 1990). Prior to its cessation, U.S. production of arsenic trioxide had been 7,300 metric tons in 1983, 6,800 metric tons in 1984, and 2,200 metric tons in 1985 (U.S. Bureau of Mines 1988). Arsenic is recovered from nonferrous ores or concentrated in at least 18 countries. In 1998, the world's largest producer of arsenic trioxide was China, followed by Chile, Ghana, Mexico, and France (USGS 1999b). China accounts for near all of the commercial-grade (99%-pure) arsenic metal production. The United States, with an apparent demand of more than 30,000 metric tons (60 million pounds) in 1998, is believed to be the worlds largest consumer of arsenic.

Table 4-1 lists facilities in each state that manufacture or process arsenic, the intended use, and the range of maximum amounts of arsenic that are stored on site. There are currently 52 large facilities that produce or process arsenic in the United States. The data listed in Table 4-1 are derived from the Toxics Release Inventory (TRI97 1999). Only certain types of facilities were required to report. Therefore, this is not an exhaustive list.

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Table 4-1. Facilities that Manufacture or Process Arsenic

State ^a	Number of facilities	Range of maximum amounts on site in pounds ^b	Activities and uses ^c
AL	4	1000-999999	8, 9
AR	1	No data	No data
CA	2	No data	No data
CO	1	No data	No data
FL	2	10000-99999	9
GA	3	1000-9999	2, 4, 8, 12
IL	3	10000-99999	1, 5, 9
IN	2	100000-999999	9
KY	2	1000-9999	8, 9
LA	1	No data	No data
MI	2	10-999999	9, 13
MN	1	10000-99999	8
MO	1	1000-9999	1, 2, 3, 4, 5, 7
MS	4	10000000-49999999	2, 3, 4, 8, 9, 10
NC	3	1000-999999	8, 9, 10
OH	1	10000-99999	1, 6
OK	1	100-999	1, 5
PA	4	1000-99999	2, 3, 7, 8, 9
SC	2	0-999999	1, 5, 9
TN	2	10000-99999	1, 3, 8, 9
TX	4	10000-99999	1, 2, 4, 6, 8
VA	2	1000-9999	8, 9
WI	1	10000-99999	8
WV	2	1000-9999	1, 3, 8, 9, 12
WY	1	100-999	1, 6

Source: TR197 1999

^aPost office state abbreviations used^bRange represents maximum amounts on site reported by facilities in each state^cActivities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct

6. Impurity
7. Reactant
8. Formulation component
9. Article component
10. Repackaging

11. Chemical processing aid
12. Manufacturing aid
13. Ancillary/other uses

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4.2 IMPORT/EXPORT

Since U.S. production ceased in 1985, all arsenic consumed in the United States is imported. Imports of arsenic have increased substantially since the mid-1980s, reaching 30,300 metric tons in 1998, of which 29,300 metric tons were as arsenic trioxide and 997 metric tons as the metal (USGS 1998b). The major exporting country is China, which supplied 54% of our arsenic imports in 1998, followed by Chile and Hong Kong with 27 and 8.6% of our imports, respectively.

U.S. exports of arsenic are minor with only 61 metric tons of arsenic metal being reported in 1997 and an estimated 40 metric tons in 1998 (USGS 1998b).

4.3 USE

Production of wood preservatives, primarily chrome copper arsenate (CCA), $\text{CrO}_3 \cdot \text{CuO} \cdot \text{As}_2\text{O}_5$, presently accounts for more than 90% of domestic consumption of arsenic trioxide. The three principal producers of arsenical wood preservatives are Hickson Corp., Smyrna, Georgia, Chemical Specialties Inc., Harrisburg, North Carolina, and Osmose Wood Preserving, Inc., Buffalo, New York (USGS 1998a). CCA is the most widely used wood preservative in the world. Wood treated with CCA is referred to as 'pressure treated' wood (American Wood Preservers Association 2000, Page and Loar 1993). In 1997, approximately 727.8 million cubic feet (20.6 million cubic meters) of wood product were pressure treated in the United States. CCA is a water-based product that protects several commercially-available species of western lumber from decay and insect attack. It is widely used in treating utility poles, building lumber, and wood foundations. CCA comes in three types, A, B, and C that contain different proportions of chromium, copper, and arsenic oxides. Type C, the most popular type, contains CrO_3 , CuO , and As_2O_5 in the proportions 47.5, 18.5, and 34.0%, respectively. The retention levels are 0.25 pounds per cubic feet (pcf) for above ground use such as fencing and decking, 0.40 pcf for lumber used in ground contact such as fence posts and deck posts, and 0.60 pcf for all weather wood foundations (Chicago Flameproof 2000; Permapost 2000). Piling used for fresh and saltwater contact should contain 0.80 and 2.5 pcf of CCA, respectively. 10,10'-Oxybisphenoxarsine (OBPA) is a leading industrial antimicrobial used primarily in the plastics industry (McEntee 1995).

Arsenic metal is used in the production of nonferrous alloys, principally lead alloys used in lead-acid batteries (USGS 1999a). Arsenic may be added to alloys used for bearing, type metal, lead ammunition,

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automotive body solder. It is also added to some brasses to improve corrosion resistance (Carapella 1992). In the past, the predominant use of arsenic was in agriculture. Organic arsenicals, namely cacodylic acid, disodium methylarsenate (DSMA), monosodium methylarsenate (MSMA), and arsenic acid are still used as herbicides (Meister 1999). Cacodylic acid is also used as a silvicide and cotton defoliant. Pesticide use data from 1992 indicates that 6.0, 1.3, and 0.14 million pounds of MSMA, DSMA, and cacodylic acid, respectively, was applied to U.S. crops; the respective area treated was 3.7, 0.76, and 0.17 million acres (Gianessi and Anderson 1995d). About 99.5% of these chemicals were applied to cotton. The remainder was applied to citrus and sod.

From the mid-nineteenth century to the introduction of organic pesticides in the 1940s, inorganic arsenic compounds were the dominant pesticides available to farmers and fruit growers. Calcium arsenate was formerly used to control the boll weevil and cotton worm and used as a herbicide. Lead arsenate was used on apple and other fruit orchards as well as on potato fields. Sodium arsenite was used to control weeds on railroad right-of-ways, potato fields, and in industrial areas, as well as in baits and to debark trees. Sodium arsenate had some application in ant traps. The use of inorganic arsenic compounds in agriculture has virtually disappeared beginning around the 1960s (Azcue and Nriagu 1994; Meister 1987; Merwin et al. 1994; Sanok et al. 1995). Food uses were voluntarily cancelled in 1993 as was the use of arsenic acid as a defoliant on cotton plants; inorganic arsenic's remaining allowable uses are in ant baits and wood preservatives (EPA 1999a, 1999h). Most agricultural uses of arsenic were banned because of concerns about human health risk during production and application or accidental poisoning at the point of use (Loebenstein 1994) (see Chapter 7). Beginning about 1975, the use of arsenic as a wood preservative began to grow, and after 1980, wood preservative uses were more important than agricultural applications. By 1990, 70% of the arsenic consumed in the United States was used by the wood preservative industry and only 20% was used by the agricultural industry (Loebenstein 1994).

High purity arsenic is used in the manufacture of gallium arsenide and other intermetallic compounds that are used in a variety of semiconductor applications including solar cells, light-emitting diodes, lasers, and integrated circuits (Carapella 1992; Sheehy and Jones 1993). Arsenic trioxide and arsenic acid were used as a decolorizer and fining agent in the production of bottle glass and other glassware. Arsenilic acid, (*p*-aminophenylarsonic acid) is used as a feed additive for poultry and swine, and sodium arsenite is used for cattle and sheep dips (Carapella 1992).

Arsenic compounds have a long history of use in medicine. Inorganic arsenic was used as a therapeutic agent through the mid twentieth century, primarily for the treatment of leukemia, psoriasis, and chronic

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bronchial asthma; organic arsenic antibiotics were extensively used in the treatment of spirochetal and protozoal disease (National Research Council 1999). The availability of inorganic arsenicals in Western medicines ended in the 1970s, although they may still be encountered in non-Western traditional medicines. By the 1980s, the only remaining medicinal organic arsenical was melarsoprol for treatment of the meningoencephalitic stage of African trypanosomiasis. Recently, there has been renewed interest in arsenic as a therapeutic agent, namely the use of arsenic trioxide in the treatment of acute promyelocytic leukemia (APL) (Gallagher 1998; Kroemer and de Thé 1999; Miller 1998).

4.4 DISPOSAL

Wastes containing arsenic are considered hazardous wastes, and as such, their treatment, storage, and disposal are regulated by law (see Chapter 7). The main route of disposal of solid wastes containing arsenic is landfilling. EPA has promulgated rules and treatment standards for landfilling liquid arsenical wastes (EPA 1990e). Other disposal alternatives for arsenic-containing wastes include incineration and recycling. There is, however, essentially no recycling of arsenic from its principal uses in wood preservatives or agricultural chemicals (IRPTC 1990; U.S. Bureau of Mines 1990). Arsenic is not recovered from consumer end product scrap, such as treated wood. This scrap will most likely be disposed of in municipal landfills or municipal waste incinerators. No arsenic is recovered domestically from nonferrous smelting, however process water and contaminated runoff from wood treatment plants are reused and gallium arsenide scrap from semiconductor devices are processed for metal recovery (USGS 1999a).

CCA treated wood is disposed of with ordinary household trash. It should not be burned in open fires, or in stoves, residential boilers, or fire places. Treated wood from commercial or industrial applications may only be burned in commercial or industrial incinerators in accordance with state and federal regulations (Hickson 2000).

According to the Toxic Chemical Release Inventory, in 1997, an estimated 53 pounds of arsenic were released by manufacturing and processing facilities to publicly owned-treatment works (POTWs) and an estimated 989,000 pounds were transferred off-site (TRI97 1999). Arsenic is listed as a toxic substance under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) under Title III of the Superfund Amendments and Reauthorization Act (SARA) (EPA 1995c). Disposal of wastes containing arsenic is controlled by a number of federal regulations (see Chapter 7).

